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(54) An acid-sensitive substance and photosensitive compositions therewith

(57) According to the present invention there is provided a polymer not comprising malic acid derivatives having acid labile groups pendant from the polymer backbone, characterized in that said pendant groups are represented by



wherein L represents a divalent linking group bonded to

the polymer backbone, R¹ represents an allyl group of which the linking C atom comprises at least one hydrogen and R² and R³ each independently represent a hydrogen or an alkyl group or R¹ and R² or R² and R³ form together a ring compound still with the proviso that the linking C atom of R¹ comprises at least one hydrogen. According to the present invention there is further provided a novel photosensitive composition comprising a latent Brönsted acid and a polymer having acid labile groups pendant from the polymer backbone as described above.

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1 End of the interview

- The present invention relates to a new group of acid-labile compounds. The present invention further relates to photosensitive compositions. The present invention still further relates to an imaging element for making a lithographic printing plate. The present invention finally relates to a method for preparing a printing plate from said imaging element.

2. Background of the invention.

Lithography is the process of printing from specially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas.

In the art of photolithography, a photographic material is made image-wise receptive to oily or greasy ink in the photo-exposed (negative working) or in the non-exposed areas (positive working) on a hydrophilic background.

In the production of common lithographic plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or oil/borne such affinity by chemical treatment is coated with a thin layer of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophilic colloids and a large variety of synthetic photocopolymers. Particularly diazo-sensitized systems are widely used.

Upon image-wise exposure of such light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.

The above-described development process can suffer from the drawbacks of being relatively time-consuming and expensive. Furthermore, when volatile organic or strongly alkaline developer solutions are used, their disposal presents an environmental problem.

What is needed in the industry is photosensitive compositions which do not have the above-described drawbacks.

A variety of different materials have been used in photosensitive compositions in the past. Photosensitive compositions employing polymers with pendant acid sensitive molecules have been described in the art (Ito, H.; Ueda, M. Macromolecules 1998, 31, 1475-82). α -Nitrobenzyl substituted polyacrylates have been described in U.S. Pat. No. 3,849,137. 1-BuM substituted polyacrylates have also been reported (Ito, H.; Wilson, C.G. in Proc. SPIE-Int. Soc. Opt. Eng. 1987, 771, 24; and U.S. Pat. No. 4,491,628).

U.S. Pat. No. 4,863,463 claims a radiation sensitive resin composition comprising an alkali-soluble resin, an α -quinones diazide, an acid-sensitive ester of nitrobenzyl or cyanobenzyl alcohol.

End-capped polyphthalaldehyde has been employed in imaging systems in combination with 'onium salts which were used as a source of photogenerated acid (Ito, H.; Wilson, C.G. Polym. Eng. Sci. 1983, 23, 1013). Phenocresols based on thermal polycarbonate degradation in the presence of chlorogenated acids have also been described (Fecht, J.M.; Bouchard, F.; Houlihan, F.M.; Kryczka, B.; Eichler, E.; Clecak, N.; Wilson, C.G. J. Imag. Sci. 1986, 30, 59). Both of these systems function by cleavage of the polymer backbone.

Canadian Patent No. 872,947 describes protective films comprising copolymers of tetrahydrophoran-2-yl acrylates, and glycidyl esters of acrylates. These films are thermally processed, thereby affecting cleavage of the tetrahydrophoran-2-yl groups, and subsequently causing cross-linking of the carboxylic acid and the epoxy residues.

Benzyl, benzoyl, and triphenylmethyl acrylates have been imaged using high energy radiation (e.g., electron beam, X-ray, and ion beam) sources followed by development with aqueous alkaline solutions as described in Japanese Kokai applications 59-075244, and 59-068743.

Dimethylbenzyl methacrylates have been employed in combination with 'onium salts as deep-UV photoresists (Ito, H. Polym. Mater. Sci. Eng. 1989, 60, 142).

α -Substituted benzyl methacrylate polymers have been photomasked and developed with an alkaline developer (Ito, H.; Ueda, M.; Etina, M. ACS Symp. Ser. 1989, 412, 57-73).

Japanese Kokai applications 63-256492 and 63-317388 describe several direct-image lithographic plate formulations employing polymers having side-chain groups which, following an etching development step, cleave to form hydroxyl and carboxyl groups.

Japanese Kodak patent applications 63-094691 and 53-100192 describe lithographic plates containing polymers with acid labile groups including some alkoxylate esters. The plates also contain cross-linking agents which appear to cross-link with carboxylic acid residues as they are formed. The plates appear to act in a negative-tone and may involve a development step.

Japanese Kokai application 62-289,313 describes the use of polymers containing acid anhydride residues in combination with α -nitrobenzyl esters of carboxylic acids. These anhydrides are selective only in UV radiation.

U.S. Pat. No. 5,102,771 discloses photosensitive compositions comprising : (a) a photoinitiator which generates an acid upon exposure to radiation; and (b) a polymer having acid labile groups pendant from the polymer backbone. These materials were combined with maleic anhydride polymers to provide increased adhesion. However, the resulting photosensitive compositions have only a moderate shelf-life under ambient conditions.

U.S. Pat. No. 5,077,174 (Bauer et al.) also discloses a positive working resist composition comprising a polymer having acid-labile pendant groups of a defined formula.

EP-A 625728 discloses a lithographic plate with an image forming layer which is UV- and IR-sensitive which can be as well positive as negative working. Said image forming layer comprises (1) a novolac resin, (2) a novolac resin, (3) latent Brønsted acid and (4) an IR absorber. By exposing with UV or IR (530 nm) light followed by a classical P-S development a positive working lithographic plate is obtained. If the plate is baked (50 seconds at 100°C) before the development step a negative working printing plate is obtained.

US-P. 4,708,925 discloses a positive working printing plate comprising a light sensitive composition comprising (1) an alkali-soluble novolak resin and an onium-salt and optionally an IR spectral sensitizing dye. By exposing with UV, visible or IR light followed by development step with an alkali solution there is obtained a positive working printing plate. There is no there is no need for acid-sensitive compounds which upon cleavage form a cationic group instead of a phenolic group so that it is possible to develop a plate comprising an acid-sensitive composition with less aggressive developers for acidic-sensitive compounds which decompose at a lower temperature.

Summary of the invention.

It is an object of the present invention to provide a new group of acid-labile compounds. It is a further object of the present invention to provide photosensitive compositions.

**It is another object of the present invention to provide an imaging element for preparing a lithographic plate being
diluted and/or heat sensitive.**

It is still another object of the present invention to provide a method for obtaining in a convenient way a positive printing lithographic printing plate of a high quality using said imaging element.

According to the present invention there is provided a polymer not comprising heteroatoms or heterocyclic groups pendant from the polymer backbone, characterized in that said pendant groups are represented by



wherein L represents a divalent linking group bonded to the polymer backbone, R¹ represents an alkyl group of which a linking C atom comprises at least one hydrogen and R² and R³ each independently represent a hydrogen or an alkyl group or R¹ and R² and R³ form together a ring compound still with the proviso that the linking C atom of

According to the present invention there is also provided a novel photosensitive composition comprising a latent image-forming agent and a photomeric bauxite, wherein neither from the colourless bauxite as mentioned above

According to the present invention there is also provided an imaging element for obtaining a lithographic printing plate comprising a hydrophilic organic base or a lithographic base, a photoresistive layer comprising a latent brominated benzene derivative and a reduction having acid labile groups, and a polymer polyacrylic acid as a protective layer.

According to the present invention there is also provided a method for obtaining a positive working lithographic printing plate comprising the steps of:

(e) Image-wise or Information-wise exposing to light or heat an imaging element as described above;

(c) developing said exposed and heated imaging element with an aqueous developing solution in order to remove the exposed areas and thereby form a lithographic printing plate.

Detailed description of the invention.

It has been found that polymers as described above yield by decomposition polymers having pendant groups comprising carbonyl functions and do so at temperatures which are clearly lower than the temperatures required for decomposition of the usual acid-labile compounds.

The polymers according to the invention are polymers having acid labile groups pendant from the polymer back-

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bone characterized in that solid dentin becomes more sclerotic by



Preparation methods 1

Biosynthesis of α -Methyl Androstan-3 β -ol by *Escherichia coli* = PRIMERA

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To a solution of 25 ml dry *t*-butanol in 80 ml THF (at 0°C) was added 80 ml butyl lithium (2.5 M in hexane) under nitrogen. After dilution of the reaction mixture with 180 ml DMF, dry CO_2 was introduced for approximately 1 hour. Next a solution of *p*-nitrobenzoyl chlorides (25 g in 25 ml DMF) was added during a period of 5 minutes. After 5 minutes of reaction time at room temperature the reaction mixture is poured out in a mixture of ice and hexanediolether (1/1, 500 ml). After extraction with saturated NaHCO_3 (2 x 250 ml), drying of the organic phase and evaporation of the solvent, the monomer is obtained. 37.2 g of the pure monomer was obtained. The monomer was characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ -spectroscopy.

Polymerisation of 4-aminobenzyl-1-butyl-carboxylic acid anhydride To a solution of 24.8 g (4-aminobenzyl-1-butyl-carboxylic acid anhydride) in 60 mL toluene was added 1.55 g of bis(4-*t*-butyl-cyclohexylcarbonyl) carbamate. Nitrogen was allowed in the reaction mixture to remove the oxygen. This solution was then shaken at 45°C for 4 hours. The polymer formed was precipitated with MeOH at -20°C. After drying at 20°C, 20.4 g (84.4 % of poly(4-aminobenzyl-1-butyl-carboxylic acid anhydride) was obtained. The polymer was characterized by IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ -spectroscopy, DSC an TGA: $M_w = 367,000$; $M_n = 24,000$; $\eta_{inh} = 114^\circ\text{C}$

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To a solution of 30 ml dry tetrahydrofuran in 200 ml *t*-butanol in 200 ml THF (at 0°C) was added 100 ml butyl lithium (2.5 M in hexane) under nitrogen. After dilution of the reaction mixture with 200 ml DMF, dry CO₂ was introduced for approximately 3 hours. Next a solution of methacryloyl chloride (33.8 g in 25 ml DMF) was added. After 5 minutes reaction time at room temperature the reaction mixture is poured out in a mixture of ice and hexane/diethylether (1/1; 500 ml). After separation with saturated NaHCO₃ (2 x 250 ml), drying of the organic phase and evaporation of the solvent, the monomer is obtained. 48.5 g of the pure monomer was obtained.

spectroscopy.

Polymerization of methacryloyl-*t*-butyl-carboxylic acid anhydride in 6 ml toluene was added 0.17 g bis(4-tert-butylidodeoxy)peroxydacetone. To a solution of 2 g methacryloyl-*t*-butyl-carboxylic acid anhydride in the reaction mixture was added nitrogen. This solution was then heated at 40°C for 1 hour. The polymer formed was precipitated with MeOH at 40°C. After drying at 0.45 g (25% of poly(methacryloyl-*t*-butyl-carboxylic acid anhydride) was obtained. The polymer was characterized by IR, ¹H-NMR, and ¹³C-NMR-spectroscopy. DSC on TGA: $M_w = 44,100$; $M_n = 24,200$; $T_{decomp} = 112^\circ\text{C}$

The differences in solubility between the exposed and unexposed areas of the photosensitive composition hydrophobic polymers may be used to increase durability or adhesion.

Exposure of the plate to radiation is believed to decompose the latent bromised acid in the exposed areas. The decomposition products are believed to decompose the polymers according to the present invention and to liberate



This second essential ingredient of the radiation-sensitive composition of this invention is a latent Bronsted acid.

that term Brønsted acid refers to a precursor which forms a Bronsted acid by decomposition. Hyper examples of Brønsted acids which are suitable for this purpose but not limited to are sulphonic acids e.g. trifluoromethane sul-

Ionic latent Bunteon acids are suitable for use in this invention. Examples of these include onium salts, in particular phosphoric acid and hexafluorophosphoric acid.

When X is iodine then R₁ and R₂ are electron lone pairs and R₃ and R₄ each independently are aryl or substituted aryl groups. When X is S or Se then R₂ is an electron lone pair and R₁, R₂ and R₄ each independently can be an aryl group, a substituted aryl group or a substituted aliphatic group. When X is P or As, then R₁, R₂, R₃ and R₄ each independently can be an aryl group, a substituted aryl group, an alkylsulfur group or a substituted aliphatic group. W can be Br⁻, Cl⁻, SO₃²⁻, CO₃²⁻, C₆H₅CO₃²⁻, AsF₆⁻, PF₆⁻ or any corresponding acid whose pH is less than three. Any of the cation salts described in U.S. Patent 4,708,925 can be utilized as the latent Bronsted acid in this invention. These include iodonium, sulfonium, phosphonium, bromonium, chloronium, oxydisulfonium, oxydisulfonium, selenonium, telluronium and arsonium salts.

Use of diazonium salts as latent Bronsted acids is particularly preferred in this invention. They provide higher sensitivity in the ultraviolet region than other latent Bronsted acids.

- 15 Specific examples of particularly useful cation salts include: diphenyliodonium hexafluorophosphate, triphenylsulfonium hexafluorantimonate, phenyliodo-*ortho*-cyanobenzylsulfonium trifluoromethane sulfonate, and 2-methoxy-4-aminophenyl diazonium hexafluorophosphate.

20 Non-ionic latent Bronsted acids are also suitable for use in this invention. Examples of these include compounds of the formula:



25 wherein X is Cl, Br, F, or CF₃SO₂ and R is an aromatic group or an aliphatic group. Further suitable non-ionic latent Bronsted acids are halocally-substituted *s*-triazines as disclosed in EP-A 672954, *o*-quinoxaline diazides, photo-acid generating agents having an *o*-nitrobenzyl-type protective group as described in Polymer Sci., by S. Hayase et al., 25, 573 (1987). The compounds which are subjected to a photodecomposition to generate a sulfonic acid, represented by iminocarbonates as described in Polymer Preprints, Japan, by M. Tunooka et al., 35 (8), by disulfone compounds described in JP-P 61-166544, by α -asaphonyl- α -ketones, by α -hydroxymethylbenzene sulfonates, by nitroso-phosphoryl sulfonates, by α -asaphonyl acetophenone ester and by sulphonil imides, the preparation of these last compounds being well known in the literature; the compounds which are subjected to a photodecomposition to generate a phosphonic acid, a partly esterified phosphoric acid or phosphoric acid, represented by nitrobenzophosphonates or phosphonates as described in Tetrahedron Letters, by M. Rubinstein et al., 17, 1445 (1975), by benzidine ethoxymethylphosphonates or phosphonates, as described in J. Org. Chem. by M. Pinting and S. Shuley, 59, 3990 (1994), by pyranethione/phosphates or phosphonates, by iminophosphates or phosphonates and by imidophosphates or phosphonates, the preparation of these last compounds being well known in the literature.

30 Further, compounds in which the above photo-sensitive acid precursors are introduced into a primary chain or a side chain of a polymer can be used. Examples thereof include the compounds described in e.g., J. Am. Chem. Soc., by M.E. Woodhouse et al., 104, 5586 (1982); U.S. Patent 3,90 (5), 218 (1969); etc. The photo-sensitive composition employed in the present invention may be either exposed to ultraviolet radiation or sensitized into the visible and/or the infrared spectrum. Wavelengths between 250 and 1500 nm may be used.

35 Compounds useful as sensitizing dyes for the visible spectrum according to this invention include, but are not limited to nitroenes, xanthenes, anthraquinones, substituted diaryl and diarylmethanes, methines, macroyanines, polymethines, thiazoles, substituted and unsubstituted polycyclic aromatic hydrocarbons such as e.g., diarykyl anthracenes, and phthalimide dyes.

40 Compounds useful as sensitizing dyes for the infrared spectrum according to this invention are infrared absorbers. The infrared absorber renders the composition sensitive to infrared radiation and makes the printing plate useful as a direct laser addressable plate which can be imaged by exposure to a laser which emits in the infrared region.

The infrared absorber can be a dye or pigment. A very wide range of such compounds is well known in the art and includes dyes or pigments of the squaramide, croconate, cyanine, merocyanine, indoline, phthalimide, diaryl and metal dithiobenzene classes. It is preferred that the infrared absorber fragments upon exposure to the activating radiation since the decomposition products promote increased contrast between image and non-image areas and thereby help in the development process.

45 Additional infrared absorbers that are of utility in this invention include those described in U.S. Patent 5, 166,924, issued November 24, 1992. As described in the '924 patent, particularly useful infrared absorbers are phthalocyanine

pigments.

As explained hereinabove, the two essential ingredients of the radiation-sensitive composition of this invention are a polymer with acid labile groups pendant from the polymer backbone according to the invention and a latent Bronsted acid. Other ingredients which can optionally be incorporated in the composition include colorants, stabilizers, additional sensitizers, exposure indicators and surfactants.

The thickness of the image forming layer in the printing plates of this invention can vary widely. Typically, a dry thickness in the range of from 0.25 to 10 micrometers, more preferably from 0.75 to 5 micrometers is suitable.

To form the radiation sensitive imaging element, the polymer with acid labile groups pendant from the polymer backbone according to the invention, the latent Bronsted acid and the other optional ingredients are dissolved or dispersed in a suitable solvent in appropriate proportions and coated on the support using such well-known coating techniques as spin coating or hopper coating. Preferred solvents include acetone, methyl ethyl ketone and 1-naphtho-2-propanol.

The polymer with acid labile groups pendant from the polymer backbone according to the invention is preferably incorporated in the coating composition in an amount of from 1.0 to 20 percent by weight, more preferably from 5 to 15 percent by weight, and most preferably from 7.0 to 13 percent by weight.

The latent Bronsted acid is preferably incorporated in the coating composition in an amount of from 0.1 to 10 percent by weight, more preferably from 0.25 to 5 percent by weight, and most preferably from 0.50 to 3.00 percent by weight.

The optional spectral sensitizer is preferably incorporated in the coating composition in an amount of from 0.1 to 3 percent by weight, more preferably from 0.15 to 2.0 percent by weight, and most preferably from 0.20 to 1.00 percent by weight.

Suitable conditions for drying the layer involve heating for a period of from 0.5 to 10 minutes at a temperature in

the range of from 20 °C to 150 °C.

According to one embodiment of the present invention, the lithographic base can be an anodised aluminum support. According to the present preferred lithographic base is an electrochemically grained and anodised aluminum support. According to the present invention, an anodised aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or can be carried out at a slightly elevated temperature of about 30 to 50°C. An interesting treatment involves treating the aluminum oxide surface with poly(mvinophenoxy) acid as disclosed in DE-OS 2,607,207. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. It is further evident that one or more of these post treatments may be carried out alone or in combination.

According to another embodiment in connection with the present invention, the lithographic base comprises a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer. A particularly suitable cross-linked hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-linking agent such as formaldehyde, glyoxal, polyisocyanates or a hydroxylated terephthaloyldiisocyanate. The latter is particularly preferred.

As hydrophilic binder there may be used hydrophilic (co)polymers such as for example, homopolymers and co-polymers of vinyl alcohol, acrylamide, methyl acrylamide, methacrylamide, acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/methylmethacrylates copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60 percent by weight, preferably 80 percent by weight.

The amount of crosslinking agent, in particular of tetraallyl orthosilicate, is preferably at least 0.2 parts by weight per part by weight of hydrophilic binder, preferably between 0.5 and 5 parts by weight, more preferably between 1.0 parts by weight and 3 parts by weight.

A cross-linked hydrophilic layer in a lithographic base used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition, finer particles of larger size than the colloidal silica can be added e.g. silica prepared according to Stober as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the cross-linked hydrophilic layer is given a uniform rough texture consisting of microscopic hills and valleys, which serve as storage places for water in background areas.

The thickness of a cross-linked hydrophilic layer in a lithographic base in accordance with this embodiment may vary in the range of 0.2 to 25 µm and is preferably 1 to 10 µm.

Particular examples of suitable cross-linked hydrophilic layers for use in accordance with the present invention

film etc... The plastic film support may be opaque or transparent.

It is particularly suitable for use as an adhesive improving layer for use in conjunction with an adhesion improving layer has been provided.

Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m² and 750 mg per m². Furthermore, the ratio of silica to hydrophilic polymer is preferably between 1 and 200, and more preferably at least 10 mg m⁻² near the surface area of the colloidal silica is preferable.

The lithographic printing plates can be exposed with conventional ultraviolet radiation sources, including carbon arc lamps, mercury vapor lamps, fluorescent lamps, and photoflood lamps. The lithographic printing plates can also be exposed with conventional ultraviolet radiation sources, including carbon arc lamps, mercury vapor lamps, fluorescent lamps, and photoflood lamps.

The lithographic printing plates of this invention when comprising both the latent Bransted acid and a laser diode which emits radiation in the near-infrared region of the spectrum. Such laser diodes provide the advantage of both low cost and low energy consumption.

DEVELOPMENT MIX-1408-1 which is sold by Eastman Kodak Company or Fuji PS-plate developer DP-5 which is sold by Fuji Camera. After contact with the aqueous alkaline developing solution, the plate is usually treated with a finishing agent such as a varnish.

The number of printing impressions obtainable is primarily dependent upon the post development baking step. If no such baking step is used, the plate typically provides 60000 to 70000 impressions, whereas post development baking for 5 minutes at 25°C typically provides 300000 to 350000 impressions. The number of impressions that can be attained before wear is defined can then be increased by increasing the coating weight.

If the imaging element of this invention is infrared sensitive, digital imaging information can be conveniently utilized to form continuous or halftone images using a suitable source of infrared radiation such as a laser diode emitting in the wavelength range of 700-1000 nm.

the infrared region. Since the printing plate of this invention is also ultraviolet sensitive, it can also be conveniently imaged so as to form continuous or halftone images by ultraviolet exposure through a suitable imaging master such as a silver halide film. Because of these characteristics, the same plate can be utilized in equipment intended for input

of electronic data by writing with a laser or in the type of equipment that is commonly employed to carry out ultraviolet exposure of lithographic printing plates. It is thus an easy matter to combine digital or electronic imaging techniques with conventional optical imaging techniques, i.e., to use both types of imaging with the same printing plate.

Information not available in an electronic format can be added by optical imaging techniques to complete the imaging of the lithographic printing plate when it is desired to do so.

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A 0.20 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using 5 g of citric acid and 4 g of hydrofluoric acid, 4 g of hydrochloric acid, 4 g of phosphoric acid and 0.5 g of oxalic acid.

aluminum ions at a temperature of 35°C and a current density of 1200 A/m² to form a surface topography with an average center-line roughness Ra of 0.5 µm.

After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 50°C for 180 seconds and rinsed with demineralized at 25°C for 30 seconds.

The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m² for about 300 seconds to form an anodic oxidation film at 3.00 g/m² of Al₂O₃, then washed with demineralized water, postratal with a solution containing 20 g/l of sodium bicarbonate at 40°C for 30 seconds, subsequently rinsed with demineralized water at 20°C during 120 seconds and dried.

10 Preparation of the lithographic printing plate

Onto the lithographic aluminum base was coated a photosensitive composition prepared by mixing 0.4 g PVBBCA (preparation example 2), 0.05 g TRIAZINE-S (2,4,6-(trichloromethyl)-s-triazine from P.C.A.S.), 0.025 g thioxonate, 0.179 g of a dye dispersion (14 % w/w HOSTAPERM BLAU B3G01 in methyl ethyl ketone) (blue dye available from HOECHST) and 4.345 g methyl ethyl ketone. This composition was coated to a wet coating thickness of 20 µm and dried. On top of the lithographic printing plate was then placed in face-to-face contact a test target with a 60 lines per cm screen as well as fine positive and negative lines, and the imaging element was exposed therethrough to ultraviolet radiation.

Next the exposed sample was heated in an oven for 5 minutes at 120°C. The heated plated was then allowed to cool to room temperature. The imaging element was then processed with Fuji PS-plate developer DP-5 to remove the exposed areas resulting in a positive working lithographic printing plate. The obtained image on the lithographic base could be used to print on a conventional offset press using a commonly employed ink and fountain. Excellent copies were obtained.

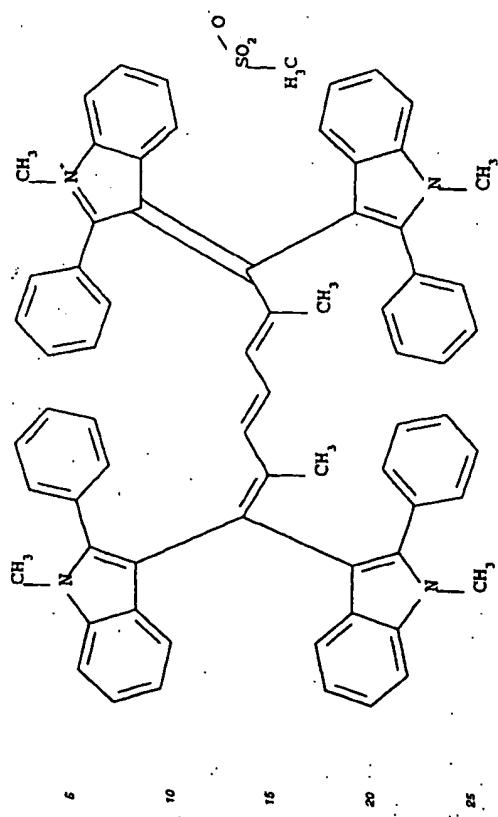
25 EXAMPLE 2

Onto the lithographic aluminum base of example 1 was coated a photosensitive composition prepared by mixing 0.4 g PVBBCA (preparation example 1), 0.05 g TRIAZINE-S (2,4,6-(trichloromethyl)-s-triazine from P.C.A.S.), 0.025 g thioxonate, 0.179 g of a dye dispersion (14 % w/w HOSTAPERM BLAU B3G01 in methyl ethyl ketone) (blue dye available from HOECHST) and 4.345 g methyl ethyl ketone. This composition was coated to a wet coating thickness of 20 µm and dried.

On top of the lithographic printing plate was then placed in face-to-face contact a test target with a 60 lines per cm screen as well as fine positive and negative lines, and the imaging element was exposed therethrough to ultraviolet radiation. Next the exposed sample was heated in an oven for 5 minutes at 120°C. The heated plated was then allowed to cool to room temperature. The imaging element was then processed with Fuji PS-plate developer DP-5 to remove the exposed areas resulting in a positive working lithographic printing plate. The obtained image on the lithographic base could be used to print on a conventional offset press using a commonly employed ink and fountain. Excellent copies were obtained.

30 EXAMPLE 3

Onto the lithographic aluminum base of example 1 was coated an IR-sensitive composition prepared by mixing 0.41 g PVBBCA (preparation example 1), 0.05 g TRIAZINE-S (2,4,6-(trichloromethyl)-s-triazine from P.C.A.S.), 0.015 g of IR-I, 0.179 g of a dye dispersion (14 % w/w HOSTAPERM BLAU B3G01 (blue dye available from HOECHST) in



35 methyl ethyl ketone) and 4,345 g methyl ethyl ketone. This composition was coated to a wet coating thickness of 20 µm. The IR-sensitive printing plate was subjected to a scanning diode-laser emitting at 830 nm (scanspeed 1.1 m/s, spot size 15 µm and the power on the plate surface was varied from 60 to 120 mW). After imaging the plate was heated in an oven for 150 seconds at 115°C and cooled to room temperature. The imaging element was then processed with Fuji PS-plate developer DP-5 to remove the exposed areas resulting in a positive working lithographic printing plate. The obtained image on the lithographic base could be used to print on a conventional offset press using a commonly employed ink and fountain. Excellent copies were obtained.

Claims

45 1. A polymer not comprising maleic acid derivatives having acid labile groups pendant from the polymer backbone, characterized in that said pendant groups are represented by



50 wherein L represents a divalent linking group bonded to the polymer backbone, R¹ represents an alkyl group of which the linking C atom comprises at least one hydrogen and R² and R³ each independently represent a hydrogen or an alkyl group or R¹ and R² or R² and R³ form together a ring compound still with the proviso that the linking C atom of R¹ comprises at least one hydrogen.

55 2. A polymer having acid labile groups pendant from the polymer backbone according to claim 1 wherein R¹, R² and R³ each independently represents a methyl or ethyl group.

3. A novel photosensitive composition comprising a latent Bronsted acid and a polymer having acid labile groups
pendant from the polymer backbone according to claim 1 or 2.
4. An imaging element for obtaining a lithographic printing plate comprising on a hydrophilic surface of a lithographic base an image forming layer comprising a latent Bronsted acid and a polymer having acid labile groups pendant from the polymer backbone according to claim 1 or 2.
5. An imaging element for obtaining a lithographic printing plate according to claim 4 wherein said latent Bronsted acid is an ionic latent Bronsted acid.
6. An imaging element according to claim 5 wherein said ionic latent Bronsted acid is an iodonium, sulphonium, selenonium, diazonium or arsonium salt.
7. An imaging element according to claim 4 wherein said latent Bronsted acid is a non-ionic latent Bronsted acid.
8. An imaging element according to claim 7 wherein said non-ionic latent Bronsted acid is a haloalkyl-substituted 9-triazine.
9. An imaging element according to any of claims 4 to 8 wherein said image forming layer comprises an ultraviolet light absorber, said ultraviolet light absorber being capable of sensitizing the decomposition of the latent Bronsted acid.
10. An imaging element according to any of claims 4 to 8 wherein said image forming layer comprises a visible light absorber, said visible light absorber being capable of sensitizing the decomposition of the latent Bronsted acid.
11. An imaging element according to any of claims 4 to 8 wherein said image forming layer comprises an infrared light absorber, said infrared light absorber being capable of sensitizing the decomposition of the latent Bronsted acid.
12. An imaging element according to any of claims 4 to 10 wherein said lithographic base is anodized aluminum or comprises a flexible support having thereon a cross-linked hydrophilic layer.
13. A method for obtaining a positive working lithographic printing plate comprising the steps of:
 - (a) image-wise or information-wise exposing to light or heat an imaging element according to any of claims 4 to 12;
 - (b) heating said exposed imaging element to provide increased solubility in the exposed areas;
 - (c) developing said exposed and heated imaging element with an aqueous developing solution in order to remove the exposed areas and thereby form a lithographic printing plate.



DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Description of document with indication, where appropriate, of relevant passages	Relevant parts of claim	Classification of the document according to ECLA
X, D	DE 42 29 816 A (JAPAN SYNTHETIC RUBBER CO., LTD.) 11 March 1993 * claims 1,6 Y * page 4 - page 7 *	1-3	6831F/039 6831F/084- B41C1/10 B41M5/36 C08F12/22 C08F20/28
Y	US 5 491 846 A (C.D. DEBOER) 13 February 1996 * column 9, line 57 - line 63; claim 19 *	4-13	
A, D	US 5 182 771 A (D.E. VOGEL ET AL.) 7 April 1992 * column 8, line 28 - line 31; claims *	4-13	
A	DE 42 25 422 A (KABUSHIKI KAISHA TOSHIBA) 4 February 1993 * page 14 - page 15 *	1-13	
			TECHNICAL FIELDS SEARCHED (ECLA)
			6831F B41C B41M C08F
			The present search report has been drawn up for all claims
Name or name THE HAGUE		Date of completion of the search 29 October 1997	Concurrent Dupart, J.-M.
CATEGORY OF CITED DOCUMENTS			
X: Infringement related & relevant, also Y: Infringement related & mentioned with another Z: Document which may be of interest A: Document cited for other reasons G: Document which may be of interest P: Document cited for other reasons B: Document which may be of interest			

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